

# Soft Chemical Modification of Blue Potassium Molybdenum Bronze

Nobukazu Kinomura,<sup>1</sup> Katsuya Mizumoto, and Nobuhiro Kumada

*Institute of Inorganic Synthesis, Faculty of Engineering, Yamanashi University, Miyamae-cho 7, Kofu, 400 Japan*

Received April 1, 1996; in revised form October 11, 1996; accepted October 24, 1996

**Hydrogen insertion compounds of general formula  $H_xK_{0.28}MoO_3 \cdot zH_2O$  have been obtained from blue potassium molybdenum bronze ( $K_{0.28}MoO_3$ ) by the spillover technique using hydrogen gas in the presence of a Pt catalyst. The hydrogen insertion compounds are formed topotactically and the original blue bronze is regenerated by standing in air for at least >2 weeks. Although the values of  $x$  exceeding approximately 0.42 could not be determined by redox titration, the value of  $x$  was estimated to be 1.3 immediately after the hydrogen insertion for about 20 h. The hydrated hydrogen insertion compound undergoes intercalation reactions with  $n$ -alkylamines. The basal spacing of the intercalation compounds increases linearly with the number of carbon atoms. The electric resistivity of the hydrogen insertion compounds was increased by the order of  $10^4$  as a result of amine intercalation.** © 1997 Academic Press

## INTRODUCTION

Blue potassium molybdenum bronze ( $K_{0.28}MoO_3$ ) shows metallic conductivity above  $\sim 180$  K (1), and much attention has focused on the highly anisotropic electrical conductivity of the blue bronze (2). The crystal structure of the blue bronze was determined by Graham and Wadsley (3) and refined by Ghedira *et al.* (4). Its incommensurately modulated structure was determined by Schutte and de Boer (5). The structure is composed of layers of  $MoO_3$  octahedra and potassium ions in the interlayer spaces. The layers are composed of subunits of 10 distorted octahedra linked by corner/edge-sharing, and the layers are stacked along the  $[20\bar{1}]$  direction.

Although the blue bronze has a layered structure, no soft chemical reactions such as ion exchange, intercalation, and deintercalation involving this phase have been reported so far. In fact our attempts of exchange  $K^+$  with other alkaline ions and proton and to deintercalate  $K^+$  by oxidation were not successful.  $MoO_3$  is used very often as a host material for various kinds of soft chemical reactions (6–8). The hydrogen insertion compound (hydrogen bronze) has been

prepared in aqueous acid solution (7) or by spillover (8) for which a H/Mo ratio of 2.0 was reported (7, 9). Furthermore, the hydrogen bronze has been reported to react topotactically with various organic Lewis bases (10). Hydrogen can also be inserted at ambient temperature into various kinds of transition metal oxides by spillover (11–13). In this paper we report the hydrogen insertion of the blue potassium molybdenum bronze and the intercalation of  $n$ -alkylamines into the hydrated hydrogen insertion compound.

## EXPERIMENTAL

### *Preparation of Potassium Molybdenum Bronze*

Polycrystalline potassium blue molybdenum bronze (BMB) was prepared as described in Ref. (14); a mixture of  $K_2MoO_4$ ,  $MoO_2$ , and  $MoO_3$  in a molar ratio of 1:1:4.67 was sealed in an evacuated silica tube and heated at  $550^\circ C$  for 1 day. The product was washed with distilled water and dried in air. The product was identified by X-ray powder diffraction (XRD) with  $CuK\alpha$  radiation (2). The composition of BMB obtained here was determined to be  $K_{0.28}MoO_3$  by atomic absorption spectroscopy and inductively coupled plasma emission spectroscopy (ICP).

### *Spillover*

Powdered  $H_2PtCl_2 \cdot 6H_2O$  (8 wt%) was added to BMB and ground well in ethanol. The mixture was dried at  $80^\circ C$  for 2 h in vacuum and exposed to a hydrogen gas stream in a reaction vessel at room temperature for 0.5–25 h. The ratio of H/Mo immediately after the hydrogen insertion was estimated by volumetric measurement using a similar apparatus mentioned by Sermon and Bond (8). The product was removed from the reaction vessel under ambient conditions except for the reaction with neat alkylamines in the vessel. As soon as the products came into contact with air, their temperature rose rapidly and the products became hydrated. After the evolution of heat ceased, samples with composition of  $H_xK_{0.28}MoO_3 \cdot zH_2O$  were used for further measurements and intercalation reactions. Determination of oxidation state of molybdenum in  $H_xK_{0.28}MoO_3 \cdot zH_2O$  was tried by redox titration with 0.1 *N* ceric sulfate solution.

<sup>1</sup> To whom correspondence should be addressed.

The mean valence of molybdenum in the samples exposed to hydrogen gas for  $\leq 3$  h was determined by the titration. However, when exposed to hydrogen gas for  $> 3$  h, the samples did not react with the ceric sulfate solution; the products were insoluble in the solution and the color of products did not fade in the solution. Therefore, the oxidation state of molybdenum for the samples exposed to hydrogen gas for  $> 3$  h could not be determined by this method, although molybdenum was expected to be reduced more than that in the sample exposed to hydrogen gas for 3 h.

### Intercalation

For the intercalation of *n*-alkylamines into  $H_xK_{0.28}MoO_3 \cdot zH_2O$  *n*-alkylamines,  $C_nH_{2n+1}NH_2$  where *n* ranges from 3 to 16 was used in acetonitrile solutions with the following concentrations: 1 M for  $n = 2-6$  and 0.1 M for  $n = 7-16$ . A powder of  $H_xK_{0.28}MoO_3 \cdot zH_2O$  which was obtained by exposure of BMB to hydrogen gas for 4 h and successive hydration was added to the solution and stirred vigorously in the temperature range of room temperature to  $60^\circ C$  for 3-7 days. The product was washed well with acetonitrile and dried in air. In order to examine the reaction of unhydrated  $H_xK_{0.28}MoO_3$  with *n*-alkylamines, neat *n*-alkylamines were introduced into the reaction vessel for the hydrogen insertion and allowed to come in contact with  $H_xK_{0.28}MoO_3$  at the temperature range of room temperature to  $60^\circ C$  for 3 days.

### Characterization

A change of the basal spacing as a result of the hydrogen insertion and intercalation was observed by XRD. The basal spacing for the intercalated samples dried at  $150^\circ C$  *in vacuo* was also measured. Thermogravimetric and differential thermal analysis (TG-DTA) was carried out at a heating rate of  $10^\circ C/min$  in air and Ar. The amounts of intercalated *n*-alkylamines were determined by elemental analysis. Species evolved on pyrolysis in a He stream were analyzed by mass spectrometry. IR spectra were recorded by a FTIR spectrometer using KBr pellets. Electric conductivity was measured by two probe method on a pressed body.

## RESULTS AND DISCUSSION

### Hydrogen Insertion

Upon exposure to hydrogen at room temperature, the color of BMB, blue with metallic luster, turned black. The adsorption of hydrogen by BMB was saturated in 20 h. The H/Mo ratio for saturation was determined to be 1.3 from the adsorbed amount of hydrogen. The H/Mo ratio for hydrogen-inserted BMB treated for 4 h was estimated to be 0.5.

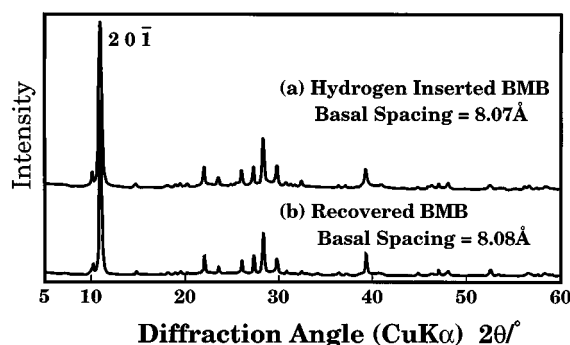


FIG. 1. XRD patterns of the hydrogen-inserted (a) and the recovered (b) BMB.

As seen in Fig. 1, the XRD pattern of products taken in air is broad, but a shift of peaks is not noticeable, when compared with that of BMB. The IR spectrum of a carefully dried sample indicated the presence of water, and a small weight loss at about  $80^\circ C$  in the TG curve shown in Fig. 2 is ascribed to release of water. Therefore, when the hydrogen-inserted BMB is exposed to air, water molecules are taken up in the interlayer space, but without an increase of basal spacing. The chemical formula of the hydrated hydrogen-inserted BMB can be expressed as  $H_xK_{0.28}MoO_3 \cdot zH_2O$ . The mean valence of Mo in the hydrated hydrogen-inserted BMB, which was exposed to hydrogen gas for 3 h and allowed to stand in air until heat evolution ceased, was reduced to 5.30 from 5.72 for the starting material, indicating the chemical formula of  $H_{0.42}K_{0.28}MoO_3 \cdot 0.45H_2O$ . As shown in Fig. 3, the oxidation state of Mo in the sample thus obtained increases gradually with time by standing in air and finally after about 2 weeks the original BMB with a sharp XRD pattern reappears. The hydrated hydrogen insertion compounds are formed topotactically from BMB and revert to the original blue bronze by prolonged exposure to air. Once the oxidation state of molybdenum exceeds 5.30, we can determine the change of the oxidation state of

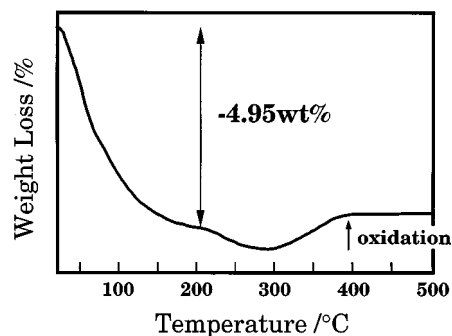


FIG. 2. TG curve for hydrated hydrogen-inserted BMB measured in air.

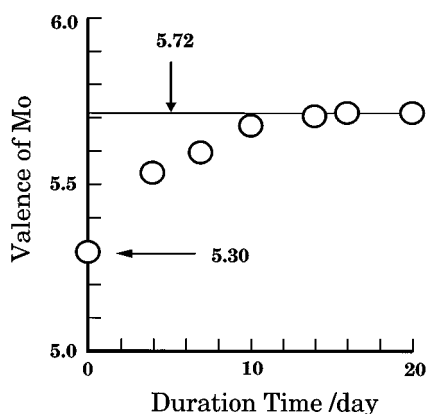


FIG. 3. Change of oxidation state of molybdenum in the hydrated hydrogen-inserted BMB obtained by exposure to hydrogen gas for 3 h with time.

molybdenum by the titration using ceric sulfate solution as mentioned above.

The amount of inserted hydrogen in  $H_xK_{0.28}MoO_3$  could be estimated from the volumetric measurement. However, the rise of temperature upon exposure to air after the hydrogen insertion causes very possibly partial oxidation of molybdenum and reduction of the amount of inserted hydrogen. Therefore, although the oxidation state of molybdenum and  $x$  in  $H_xK_{0.28}MoO_3 \cdot zH_2O$  used for the intercalation reactions are expected to be  $< 5.30$  and  $> 0.42$ , their exact values remain ambiguous. It is thought that the reactivity of  $H_xK_{0.28}MoO_3 \cdot zH_2O$  to the ceric sulfate solution is a good indicator for estimating the oxidation state of molybdenum, whether it is  $< 5.30$  or not.

#### Intercalation of *n*-Alkylamines

The hydrogen-inserted BMB removed under ambient conditions can react with *n*-alkylamines with  $n \geq 4$ , and an increase of basal spacing is observed, accompanied by a large macroscopic increase in volume. When  $n \leq 3$ , samples were dissolved. However the hydrogen-inserted BMB which stayed in the reaction vessel without exposure to moisture revealed no reactivity to *n*-alkylamines. It is necessary for the hydrogen-inserted BMB to be hydrated in order to intercalate *n*-alkylamines into the interlayer space. Therefore, the inserted hydrogen atoms are considered to exist as hydronium ions in the interlayer space of the hydrated hydrogen-inserted BMB and react as acid with the Lewis base, *n*-alkylamines, in the intercalation reaction.

Although a variation of the basal spacing was observed during the intercalation of alkylamine, prolonged treatment resulted in products with a constant basal spacing. Since potassium ions remain in the interlayer space, the composition of the intercalation compounds can be represented as  $(C_nH_{2n+1}NH_2)_yH_xK_{0.28}MoO_3 \cdot zH_2O$ . In Table 1, the

TABLE 1  
Basal Spacings,  $y$  and  $z$  Values for  
 $(C_nH_{2n+1}NH_2)_yH_xK_{0.28}MoO_3 \cdot zH_2O$

| $n$ | Basal Spacing (Å) | $y$  | $z$ |
|-----|-------------------|------|-----|
| 4   | 16.13             | 0.60 | 3.7 |
| 5   | 17.28             | 0.54 | 2.6 |
| 6   | 18.65             | 0.56 | 3.2 |
| 7   | 20.82             | 0.51 | 2.3 |
| 8   | 23.26             | 0.60 | 3.0 |
| 9   | 25.41             | —    | —   |
| 10  | 26.97             | 0.55 | 1.6 |
| 11  | 30.97             | 0.53 | 1.8 |
| 12  | 30.79             | 0.75 | 2.1 |
| 13  | 32.91             | —    | —   |
| 14  | 34.87             | 0.59 | 1.4 |
| 15  | 33.38             | 1.54 | 4.4 |
| 16  | 36.96             | —    | —   |

values of  $y$  and  $z$  and the basal spacing are listed. Based upon the facts that the intercalation of *n*-alkylamines into hydrated hydrogen-inserted BMB is an acid–base reaction and the amounts of alkylamines, except  $n = 12$  and  $15$ , are almost comparable to that of inserted hydrogen  $> 0.42$ , most of the alkylamine molecules are considered to be protonated in the interlayer space. In fact absorption at about  $1560\text{ cm}^{-1}$  in the IR spectra of intercalated compounds reveals the existence of ammonium ions in the interlayer space (15). In contrast to reversion of  $H_xK_{0.28}MoO_3 \cdot zH_2O$  to  $K_{0.28}MoO_3$  by standing in air, the XRD pattern of the alkylamine intercalation compounds was preserved even after several months in air and intact to the ceric sulfate solution. This fact indicates probably that the oxidation state of molybdenum was kept to  $< 5.30$ . It appears that the intercalation of *n*-alkylamines stabilizes the reduced state of molybdenum in  $(C_nH_{2n+1}NH_2)_yH_xK_{0.28}MoO_3 \cdot zH_2O$ .

The basal spacings of *n*-alkylamine intercalated compounds and samples dried at  $150^\circ\text{C}$  are plotted vs carbon number in Fig. 4. As seen in this figure, the basal spacing

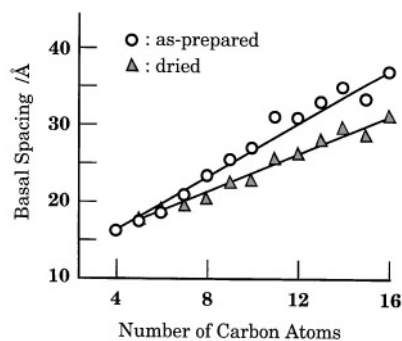


FIG. 4. Change of the basal spacing of the as-prepared (○) and dried (△) *n*-alkylamine intercalation compounds.

shrinks by removal of a part of  $n$ -alkylamines on drying, and the shrinkage increases with the carbon number. From the slope of the line ( $1.80 \text{ \AA}/C$ ) for the as-prepared intercalated compounds, alkyl chains in the interlayer space are considered to form a bilayer arrangement of all-trans alkyl chains with a tilt angle of  $45.1^\circ$  to the  $MoO_3$  layer. An intercept of  $8.82 \text{ \AA}$  at  $n = 0$  for the as-prepared intercalated compounds corresponds to the basal spacings of BMB and hydrated hydrogen-inserted BMB. Assuming a similar bilayer arrangement for dried samples, a tilt angle of  $30.0^\circ$  is calculated from the slope of  $1.27 \text{ \AA}/C$ . These values are unusually small for bilayer arrangements of all-trans alkyl chains. The line for the dried samples gives an intercept of  $10.8 \text{ \AA}$  at  $n = 0$ , which is much larger than the basal spacings of BMB and hydrated hydrogen-inserted BMB. When all-trans alkyl chains are packed regularly in the interlayer space, a stepwise increase of the basal spacing with  $n$  is observed; the increments from  $n = \text{even}$  to  $n = \text{odd}$  are larger than from  $n = \text{odd}$  to  $n = \text{even}$  (16). In the case of the regular paraffin-like arrangement of alkyl chains with a very low tilt angle  $\leq 34.5^\circ$ , the negative increments from  $n = \text{odd}$  to  $n = \text{even}$  should be observed (17). However, despite the supposed tilt angle of  $30^\circ$ , such a regular change of the basal spacing is not seen for the dried samples as shown in Fig. 4. Therefore, the alkyl chains in the dried samples are considered to be arranged irregularly with less dense packing in the interlayer space than before drying and the kink-block and/or gauche-block would exist in the alkyl chains in the interlayer space of dried samples (18).

Attempted intercalation of pyridine into the hydrated hydrogen-inserted BMB was not successful. This result indicates that the acidity of this compound is lower than that of the hydrogen bronze of  $H_{0.5}MoO_3$  reported by Schöllhorn *et al.* (10). In addition to this difference, it is interesting to note that the hydrogen-inserted BMB must be hydrated in order for the intercalation of  $n$ -alkylamines to take place. On the other hand the hydrogen atoms in  $H_{0.5}MoO_3$ , which is ready to intercalate organic Lewis bases without water molecules in the interlayer space, were supposed to form Mo–O–H bonds on the interlayer surface (10). The fact that unhydrated hydrogen-inserted BMB did not intercalate  $n$ -alkylamines may indicate that the inserted hydrogen atoms are not positioned on the interlayer surface or that the acidity of O–H in the hydrogen-inserted BMB is too weak to react with  $n$ -alkylamines. In the case of the hydrated hydrogen-inserted BMB, it is thought that upon hydration the inserted hydrogen atoms form hydronium ions with water molecules, and the hydronium ions are located in the gap between the  $MoO_3$  layers and then can react with  $n$ -alkylamines.

The  $n$ -hexylamine intercalation compound is practically an insulator with electric resistivity of about  $4.5 \times 10^7 \Omega \cdot \text{cm}$  at room temperature, whereas the hydrated hydrogen insertion compounds are semiconductors above liquid  $N_2$  tem-

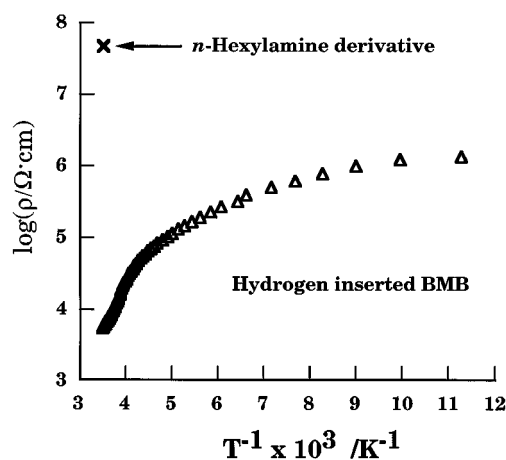


FIG. 5. Electric resistivity of the hydrated hydrogen-inserted BMB and  $n$ -hexylamine derivative.

perature as shown in Fig. 5, having an electric resistivity of about  $5.3 \times 10^3 \Omega \cdot \text{cm}$  at room temperature. As mentioned above, BMB is known as a typical compound with low dimensional metallic conductivity at room temperature. It is difficult to compare the electric resistivity of the hydrated hydrogen-inserted BMB or the  $n$ -hexylamine intercalation compound with that for BMB, because our measurement was performed on pressed bodies. However, assuming that the framework of layers for BMB is substantially preserved after the hydrogen insertion and intercalation reactions, the increase of electric resistivity by more than some four orders of magnitude for the intercalation compound may be ascribed to the much larger separation of the  $MoO_3$  layers in the intercalation compound than that in BMB. It would be interesting to see, if orientated samples could be obtained somehow, if the conductivity along the  $MoO_3$  chains (along the  $b$  crystallographic axis) in the layer remains high (and metallic?).

#### ACKNOWLEDGMENTS

This research was supported by Grant-in-Aid for Scientific Research (B) (07455440) from the Ministry of Education, Science and Culture, Japan.

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